

What is claimed is:

1. A process for forming a substantially transparent, abrasion-resistant film from a film-forming composition containing surface-treated nanocrystalline particles dispersed in a cross-linkable resin, the process comprising the steps of:
 - (a) adding nanocrystalline particles to a medium, said nanocrystalline particles being selected from the group consisting of ceramics and metals;
 - (b) mixing the nanocrystalline particles and medium to form a dispersion;
 - (c) adding a surface treatment solution to the nanocrystalline particle dispersion, said surface treatment solution comprising one or more siloxane species;
 - (d) mixing the nanocrystalline particle dispersion with the surface treatment solution such that said one or more siloxane species are disposed at the surface of at least some of said particles, whereby at least some surface-treated nanocrystalline particles are obtained;
 - (e) adding said surface-treated nanocrystalline particles to a cross-linkable resin to form a film-forming composition;
 - (f) applying said film-forming composition to a substrate;

- (g) forming a substantially transparent, abrasion-resistant film on said substrate from said film-forming composition.

2. The process of claim 1 wherein the nanocrystalline particles comprise materials selected from the group consisting of the oxides of aluminum, titanium, zinc, cerium, tin,
5 antimony, indium, iron, strontium, barium, and yttrium, mixed oxides comprising any of the foregoing elements, and combinations and mixtures of any of the foregoing oxides.

3. The process of claim 1 wherein the nanocrystalline particles comprise materials selected from the group consisting of oxides of aluminum, titanium, zinc, and cerium, mixed oxides
5 comprising any of the foregoing elements, and combinations and mixtures of any of the foregoing oxides.

4. The process of claim 1 wherein the nanocrystalline particle dispersion has a concentration of the nanocrystalline particles in the range of from about 5 percent by weight to
5 about 40 percent by weight.

5. The process of claim 1 wherein the film-forming composition is applied to the substrate at a thickness of less than about 2 mils.

6. The process of claim 1 wherein the film-forming composition is applied to the substrate at a thickness of about 1 mil.

7. The process of claim 1 wherein said surface treatment solution is prepared from one or more silane monomers defined by Formula I, wherein Formula I is $R_nSi(OR')_{4-n}$, wherein

5 R is a hydrocarbyl entity, optionally containing one or more functional groups,

R' is a hydrocarbyl entity, optionally containing one or more functional groups, and

n is 0, 1, 2, or 3.

8. The process of claim 7 wherein R further comprises one or more functional groups selected from the group consisting of saturated or unsaturated alkyl, aromatic, alcohol, aldehyde,
5 ester, epoxide, carboxylic acid, ether, ketone, amine, sulfonate, thiol, phosphine, phosphate, cyanate, isocyanate, fluoro, and pyridine.

9. The process of claim 7 wherein the surface treatment solution is prepared from at least four silanes, with at least one silane selected from the group defined by Formula I when
5 n is 0, at least one silane selected from the group defined by Formula I when n is 1, at least one silane selected from the group defined by Formula I when n is 2, and at least one silane selected from the group defined by Formula I when
10 n is 3.

10. The process of claim 9 wherein said at least four silanes react to form a siloxane star-graft polymer.

11. The process of claim 1 wherein the surface treatment solution comprises

a siloxane-based polymer comprising the reaction product of tetrafunctional,
5 trifunctional, difunctional, and monofunctional silane monomers,

wherein w, x, y and z represent the mole percent of the tetrafunctional, trifunctional, difunctional and monofunctional monomeric units,
10 respectively, and

wherein w is from about 20 to about 100, and x is from 0 to about 30, y is from 0 to about 50, and z is from 0 to about 10, respectively, and at least one of x, y and z is greater than zero.

12. The process of claim 11 wherein said siloxane-based polymer comprises the reaction product of at least one tetrafunctional silane monomer, at least one trifunctional silane
5 monomer, at least one difunctional silane monomer, and at least one monofunctional silane monomer.

13. The process of claim 12, wherein said at least one tetrafunctional silane monomer is tetraethylorthosilicate;
said at least one trifunctional silane
5 monomer is selected from the group consisting of γ -

glycidoxypropyltrimethoxysilane, n-hexyltrimethoxysilane, isobutyltrimethoxy-silane, γ -methacryloxypropyltrimethoxysilane, n-octadecyltrimethoxysilane, and n-propyltrimethoxysilane;

10 said at least one difunctional silane monomer is selected from the group consisting of dicyclohexyldimethoxysilane, diethyldiethoxysilane, dimethyldichlorosilane, 15 dimethyldiethoxysilane, dimethyldimethoxysilane, diphenyldiethoxysilane, diphenyldimethoxy-silane, di-n-hexyldichlorosilane, n-hexyl-methyldichlorosilane, methyldodecyldiethoxysilane, neophylmethyldimethoxysilane, and n- 20 octylmethyldimethoxysilane; and

 said at least one monofunctional silane monomer is selected from the group consisting of n-octadecyldimethylmethoxysilane, triethylsilanol, trimethylethoxysilane, and trimethylmethoxysilane.

14. The substantially transparent, abrasion-resistant film formed by the process of claim 13.

5 15. The process of claim 1, wherein the cross-linkable resin is selected from the group consisting of acrylics, aminoplasts, urethanes, carbamates, carbonates, polyesters, epoxies, silicones, and polyamides.

16. The process of claim 1, wherein the cross-linkable resin is selected from the group

consisting of aminoplasts, urethanes, carbamates, carbonates, polyesters, silicones, and polyamides.

17. The substantially transparent, abrasion-resistant film formed by the process of claim 1.

18. A substantially transparent, abrasion-resistant film comprising a cross-linked resin and a plurality of surface-treated nanocrystalline particles' dispersed in said cross-linked resin,
5 said surface-treated nanocrystalline particles comprising nanocrystalline particles and at least one siloxane species disposed at the surface of at least some of said particles, wherein said nanocrystalline particles are selected from the
10 group consisting of ceramics and metals.

19. The substantially transparent, abrasion-resistant film of claim 18 wherein said at least one siloxane species comprises a siloxane star-graft coating polymer.

20. The substantially transparent, abrasion-resistant film of claim 18 wherein said at least one siloxane species comprises a siloxane-based
5 polymer, and

said siloxane-based polymer comprises the reaction product of tetrafunctional, trifunctional, difunctional, and monofunctional silane monomers,

10 wherein w, x, y and z represent the mole percent of the tetrafunctional, trifunctional,

difunctional and monofunctional monomeric units, respectively, and

wherein w is from about 20 to about 100, and
15 x is from 0 to about 30, y is from 0 to about 50,
and z is from 0 to about 10, respectively, and at
least one of x, y and z is greater than zero.

21. The substantially transparent, abrasion-resistant film of claim 20 wherein said cross-linked resin is the product of at least one cross-linkable resin selected from the group consisting
5 of acrylics, aminoplasts, urethanes, carbamates, carbonates, polyesters, epoxies, silicones, and polyamides.

22. The substantially transparent, abrasion-resistant film of claim 20 wherein said cross-linked resin is the product of at least one cross-linkable resin selected from the group consisting
5 of aminoplasts, urethanes, carbamates, carbonates, polyesters, silicones, and polyamides.

23. The substantially transparent, abrasion-resistant film formed of claim 20, wherein said film has a hardness of 2B or harder, as measured by the ASTM D3363 Pencil Test.

24. The substantially transparent, abrasion-resistant film formed of claim 20, wherein said film has a percent haze less than about 14%.

25. The substantially transparent, abrasion-

resistant film formed of claim 20, wherein said film has a percent haze less than about 1%.

26. A process for making a film-forming composition containing surface-treated nanocrystalline particles dispersed in a cross-linkable resin, said film-forming composition
5 being suitable for forming a transparent, abrasion-resistant film, said process comprising the steps of:

- 10 (a) adding nanocrystalline particles to a medium, said nanocrystalline particles being selected from the group consisting of ceramics and metals;
- (b) mixing the nanocrystalline particles and medium to form a dispersion;
- 15 (c) adding a surface treatment solution to the nanocrystalline particle dispersion, said surface treatment solution comprising at least one siloxane species;
- 20 (d) mixing the nanocrystalline particle dispersion with the surface treatment solution such that said at least one siloxane species is disposed at the surface of at least some of said plurality of particles, whereby surface-
25 treated nanocrystalline particles are obtained;
- (e) adding said surface-treated nanocrystalline particles to a cross-linkable resin to form a film-forming

30 composition;
wherein a cross-linkable film-forming
composition is formed.

27. The process of claim 26 wherein the
nanocrystalline particles comprise materials
selected from the group consisting of the oxides
of aluminum, titanium, zinc, cerium, tin,
5 antimony, indium, iron, strontium, barium, and
yttrium, including mixed oxides, and combinations
or mixtures of any of the foregoing oxides.

28. The process of claim 26 wherein the
nanocrystalline particles comprise materials
selected from the group consisting of oxides of
aluminum, titanium, zinc, and cerium, and mixtures
5 thereof.

29. The process of claim 26 wherein the
nanocrystalline particles and the medium are mixed
by a method selected from stirring, high-shear
mixing, ultrasonic vibration, and blending in a
5 media mill.

30. The process of claim 26 wherein the
nanocrystalline particle dispersion has a
concentration of the nanocrystalline particles in
the range of from about 0.1 percent by weight to
5 about 75 percent by weight.

31. The process of claim 26 wherein the
nanocrystalline particle dispersion has a

concentration of the nanocrystalline particles in the range of from about 1 percent by weight to
5 about 50 percent by weight.

32. The process of claim 26 wherein the nanocrystalline particle dispersion has a concentration of the nanocrystalline particles in the range of from about 5 percent by weight to
5 about 40 percent by weight.

33. The process of claim 26 wherein said surface treatment solution is prepared from one or more silane monomers defined by Formula I, wherein Formula I is $R_nSi(OR')_{4-n}$, wherein
5 R is a hydrocarbyl entity, optionally containing one or more functional groups,
R' is a hydrocarbyl entity, optionally containing one or more functional groups, and
n is 0, 1, 2, or 3.

34. The process of claim 33 wherein
R further comprises one or more functional groups selected from the group consisting of saturated or unsaturated alkyl, aromatic, alcohol,
5 aldehyde, ester, epoxide, carboxylic acid, ether, ketone, amine, sulfonate, thiol, phosphine, phosphate, cyanate, isocyanate, fluoro, and pyridine; and
R' is an alkyl group.

35. The process of claim 26 wherein the surface treatment solution is prepared from at

least four silanes, with at least one silane
selected from the group defined by Formula I when
5 n is 0, at least one silane selected from the
group defined by Formula I when n is 1, at least
one silane selected from the group defined by
Formula I when n is 2, and at least one silane
selected from the group defined by Formula I when
10 n is 3.

36. The process of claim 35 wherein said at
least four silanes react to form a siloxane star-
graft polymer.

37. The process of claim 26 wherein said at
least one siloxane species comprises

a siloxane-based polymer comprising the
reaction product of tetrafunctional,
5 trifunctional, difunctional, and monofunctional
silane monomers,

wherein w, x, y and z represent the mole
percent of the tetrafunctional, trifunctional,
difunctional and monofunctional monomeric units,
10 respectively, and

wherein w is from about 20 to about 100, and
x is from 0 to about 30, y is from 0 to about 50,
and z is from 0 to about 10, respectively, and at
least one of x, y and z is greater than zero.

38. The process of claim 37 wherein said
siloxane-based polymer comprises the reaction
product of at least one tetrafunctional silane
monomer, at least one trifunctional silane

5 monomer, at least one difunctional silane monomer,
and at least one monofunctional silane monomer.

39. The process of claim 38, wherein
said at least one tetrafunctional silane
monomer is tetraethylorthosilicate;

said at least one trifunctional silane
5 monomer is selected from the group consisting of γ -
glycidoxypropyltrimethoxysilane, n-
hexyltrimethoxysilane, isobutyltrimethoxy-silane,
 γ -methacryloxypropyltrimethoxysilane, n-
octadecyltrimethoxysilane, and n-
10 propyltrimethoxysilane;

said at least one difunctional silane monomer
is selected from the group consisting of
dicyclohexyldimethoxysilane,
diethyldiethoxysilane, dimethyldichlorosilane,
15 dimethyldiethoxysilane, dimethyldimethoxysilane,
diphenyldiethoxysilane, diphenyldimethoxy-silane,
di-n-hexyldichlorosilane, n-hexyl-
methyldichlorosilane, methyldodecyldiethoxysilane,
neophylmethyldimethoxysilane, and n-
20 octylmethyldimethoxysilane; and

said at least one monofunctional silane
monomer is selected from the group consisting of
n-octadecyldimethylmethoxysilane, triethylsilanol,
trimethylethoxysilane, and trimethylmethoxysilane.

40. The film-forming composition made by the
process of claim 39.

41. The process of claim 26, wherein said

film-forming composition comprises a discontinuous phase, and said cross-linkable resin is disposed in said discontinuous phase.

42. The process of claim 26, wherein said film-forming composition comprises an emulsion.

43. The film-forming composition made by the process of claim 26.

44. A film-forming composition comprising a cross-linkable resin and a plurality of surface-treated nanocrystalline particles dispersed in said cross-linkable resin, said surface-treated
5 nanocrystalline particles comprising nanocrystalline particles and at least one siloxane species disposed at the surface of at least some of said plurality of particles, wherein said nanocrystalline particles are selected from
10 the group consisting of ceramics and metals.

45. The film-forming composition of claim 44 wherein said siloxane species comprises a siloxane-based polymer

46. The film-forming composition of claim 45 wherein said siloxane-based polymer comprises a siloxane star-graft coating polymer.

47. The film-forming composition of claim 44 wherein

said siloxane-based polymer comprises the
reaction product of tetrafunctional,
5 trifunctional, difunctional, and monofunctional
silane monomers,

wherein w, x, y and z represent the mole
percent of the tetrafunctional, trifunctional,
difunctional and monofunctional monomeric units,
10 respectively, and

wherein w is from about 20 to about 100, and
x is from 0 to about 30, y is from 0 to about 50,
and z is from 0 to about 10, respectively, and at
least one of x, y and z is greater than zero.

48. The film-forming composition of claim 44
wherein said cross-linkable resin is selected from
the group consisting of acrylics, aminoplasts,
urethanes, carbamates, carbonates, polyesters,
5 epoxies, silicones, and polyamides.

49. The film-forming composition of claim 44
wherein said cross-linkable resin is selected from
the group consisting of aminoplasts, urethanes,
carbamates, carbonates, polyesters, silicones, and
5 polyamides.

